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The Specific Organic Reagents of Analytical Chemistry

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Tschuegaev, in 1905, reported that an organic compound, dimethylglyoxime, could be used to precipitate nickel from an aqueous solution. However, specific organic reagents have been used extensively for inorganic analysis only within the last two decades. Researches made during that period demonstrated the individual properties of metallic ions with relation to organic compounds that possess a certain atomic grouping. Thus, the 1,2-dioxime grouping of dimethylglyoxime, which results in the formation of the well-known red precipitate with nickel ions, is characteristic of all antidioximes of the 1,2-diketone type. Many other organic reagents also react similarly with metallic ions to form complex salts, of which there are several classes.

Types of Complex Compounds

The complex compounds can be classified into three main groups: (1) addition, (2) penetration, and (3) inner.

Addition- and penetration-complex compounds are formed in such a manner that a central atom co-ordinates several atoms or polar molecules, the number of which constitutes the co-ordination number. They are bound to the central atom by principal and co-valence bonds. The addition-complex compounds are further characterized by the fact that the direct union between the cation and anion remains unchanged, whether in the solid or dissolved state. These compounds, in general, exhibit the properties of non-electrolytes. An example is the complex compound of pyridine and chromic chloride [$CrCl_3 \cdot 3$ Pyridine].

Another example of the addition-type complex is found in the union of ferrous iron with α,α'-dipyridyl or o-phenanthroline. Six co-ordination positions of the ferrous ion are occupied by three molecules of the base, each with two nitrogen atoms. The grouping is highly specific for the ferrous ion and remains so unless negative substituents are introduced into the parent molecule.

The term "penetration compound" arises from the fact that the "co-ordinatant" enters between the cationic constituent (central atom) and the anionic constituent, and thus loosens the bond between the two. An example is copper tetramine sulfate—

$$CuSO_4 + 4\ NH_3 = \begin{bmatrix} NH_3 & & NH_3 \\ & Cu & \\ NH_3 & & NH_3 \end{bmatrix}^{++} SO_4^{--}$$

The ammonia molecules, but not the sulfate ion, are bound complexly to the copper ion.

The inner-complex compounds are encountered more frequently in analytical

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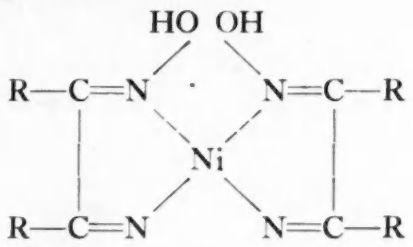
chemistry than either the addition- or the penetration-type, and for this reason will be discussed in greater detail in this article.

The formation of an inner-complex compound occurs when the metallic atom of an organic salt is co-ordinated to a second atom of the same molecule, resulting in a ring structure. The stability of the heterocyclic ring is in agreement with the Baeyer tension theory. Organic compounds forming inner complexes must not only possess co-ordinating atoms, but also salt-forming groups such as carboxyl, hydroxyl, sulfonic acid, sulfinic acid, sulfhydryl, oxime, imido, or amino. The selective action of the organic reagents toward certain metallic ions is due largely to the co-ordinating atoms and salt-forming groups, but the remaining portion of the molecule also plays its part. Further, the inner-complex compounds depend for ring closure on the nature of the metal atom itself. Consequently, many individual properties of the metals that are not observed in their normal salts appear upon the formation of inner-complex compounds. From the analytical standpoint this consideration is of great importance for the selective or specific action of organic reagents.

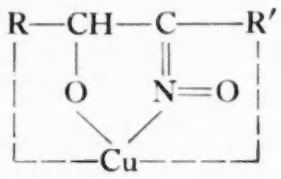
Some Inner-complex Salts

Numerous α-dioximes react with nickel salts to form an insoluble, red inner-complex compound that has the following structure—



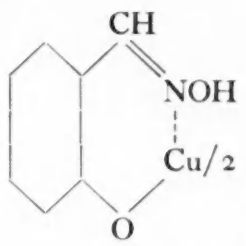
The second hydroxyl group of the dioxime plays no role in the formation of the inner complex, as can be seen from the fact that if the second oxime group is changed to the corresponding imino, methoxy imino, methyl imino, or ketonic group, the characteristic red inner-complex salt is still formed. The α-dioximes lose their specificity toward nickel, however, if a benzenoid ring is introduced, as in o-benzoquinone dioxime and o-naphthoquinone dioxime. The specificity returns when the double bonds of the benzenoid ring have been saturated, as in cyclohexanedionedioxime. Strictly speaking, the dioxime grouping is only one arrangement of the true nickel-binding group. Inner-complex nickel salts are formed with each of the following compounds—2-pyridyl methyl ketoxime, 2-pyridyl phenyl ketoxime, and nitroso guanidine. It is concluded, then, that the nickel complex is formed by the union of nickel with two nitrogen atoms by means of one principal and one auxiliary valence, with the resulting formation of a five-membered ring.

Of the acyloin oximes, the α-benzoin oximes are the so-called copper-specific compounds, forming complexes of the following type—



The inner-complex compounds are formed with copper only when the R and R′ groups can co-ordinately saturate the copper atom; otherwise, the acyloin oximes react only as dibasic acids toward copper. If R and R′ represent aromatic radicals with or without ring substituents, free amino groups, or the higher aliphatic radicals, the copper atom can be co-ordinated suitably.

Salicylaldoxime, a specific reagent for copper, forms complex salts of the following type—

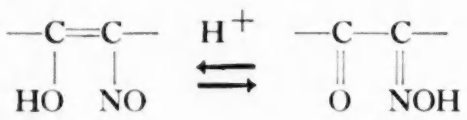


The specific group in salicylaldoxime differs from the usual copper-specific group of the acyloin oximes in that an

extra carbon atom lies between the oxime and hydroxyl groups. The introduction of one more carbon atom between these groups causes the compound to lose its specificity for copper.

The formation of inner-complex salts is dependent on the nature of the metal atom, as is shown by the fact that the copper salt of amino acetic acid is a typical inner-complex salt, while the zinc and cadmium salts are not, even though a co-ordination of ammonia with these two metal salts exists in numerous other compounds. On the other hand, the cyclic compound α-picolinic acid, which contains a grouping similar to that of amino acetic acid, does not form inner-complex salts with copper. Nevertheless, with ferrous salts, the α-picolinic-type compounds always produce soluble, colored inner-complex salts.

Both α-nitroso-β-naphthol and β-nitroso-α-naphthol are of interest in the analytical chemistry of cobalt. The inner-complex salts of cobalt with the nitroso naphthols are derived from the tautomeric quinone and oxime forms. These salts are formed in weakly acid, neutral, or ammoniacal solutions because the nitroso naphthols, as tautomeric compounds, exist in two forms in equilibrium with each other—



In strong acid the equilibrium lies toward the phenolic form, in which case the formation of the cobalt complex is impossible. Once formed, however, the complex salts of cobalt and nitroso naphthols are insoluble even in mineral acids.

Among the numerous substances containing the imino group, rhodanine and its derivatives are the outstanding reagents. They form a four-membered chelate ring with silver ions. The parent form (rhodanine) can give rise to three enol or tautomeric sulfhydryl forms through the shifting of one hydrogen atom. By stepwise substitution, so that each enolization possibility is eliminated, it has been shown that the inner-complex salt of silver is formed by the parent keto form. Rhodanine will condense through the active methylene with p-dimethylaminobenzaldehyde to form p-dimethylaminobenzalrhodanine, which is a very sensitive and highly selective reagent for the determination of silver.

Applications

The advantage of these organic reagents in analytical practice lies in the fact that the inner complexes possess an organic character which manifests itself by the persistence of their solubility in organic solvents and their insolubility in aqueous solutions. The importance to the analytical chemist of solubility relationships of compounds need not be stressed; and of no less importance is the fact that inner-complex compounds are frequently colored. The high molecular weight of the organic reagents promotes a favorable conversion factor for the metal determined, thus permitting analysis for small quantities of metallic ions.

The ideal reagent is approached by those compounds that have a definite specificity for one metallic ion under a given experimental environment. Dimethylglyoxime has this type of specificity for nickel. Reagents are also available that will precipitate several ions simultaneously, under fixed experimental conditions, such as oxine (8-hydroxyquinoline), cupferron (ammonium nitrosophenylhydroxylamine), and dithizone (diphenylthiocarbazone). These are valuable for group separations, as well as for individual determinations when conditions are favorable. Many reagents are of this type. Their value lies in the fact that usually all ions that are precipitatable by them are not present together. When they occur simultaneously, separation may be effected by means of an independent chemical method or even by a second organic reagent. In short, the success of such separations and determinations

lies in the proper selection of the best methods of procedure.

Organic reagents have recently been employed in amperometric titrations in addition to their use in the routine gravimetric or colorimetric procedures of analytical chemistry. The amperometric titrations of nickel with dimethylglyoxime and of cobalt with α-nitroso-β-naphthol have been shown to be specific, rapid, and accurate methods for determining even micro quantities of these metals.

General References

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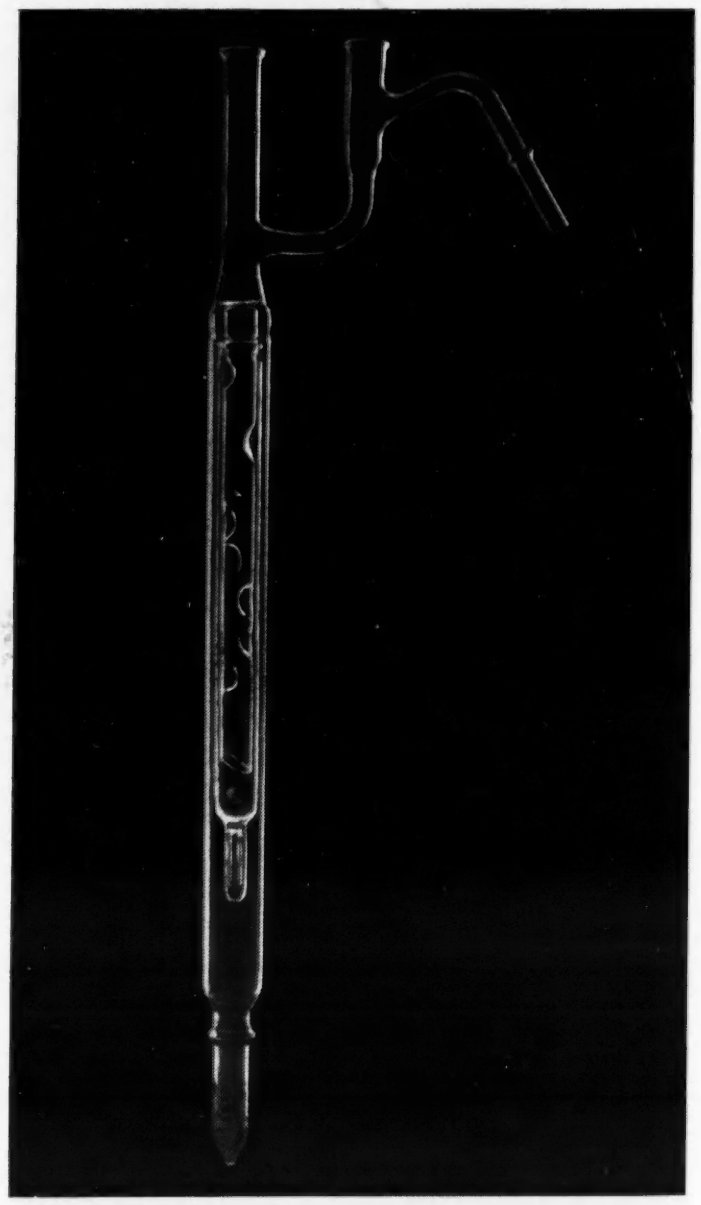
A Fractionation Column

THE ACCOMPANYING ILLUSTRATION shows a compact laboratory fractionation column that is especially convenient on a bench or where the available height is restricted. It consists essentially of three concentric tubes that form a vapor passage, which is three times the length of the column. The center tube is indented in a spiral pattern in order to lengthen the vapor path and to produce better contact between the vapors and the reflux. This tube is an adaptation of the well-known Widmer column, but it is more practical because there are no loose parts which can become broken easily during cleaning or while in use. A liquid trap is incorporated at the lower end of the second tube. This trap also consists of three concentric tubes, the outer one of which serves as an insulator that tends to keep the low-boiling condensate from being boiled away by the ascending hot vapors. The amount of reflux in the column is regulated by changing the height of the dephlegmator.

The vapors first pass upward between the walls of the outer and second tubes. At the top, they enter the space between the second and innermost tubes, through several small openings, and flow downward. They then pass upward, spirally, through the central tube to the condenser. Condensate from the second and third tubes flows through the liquid trap.

This column can be built in various sizes ranging from the large one illustrated that is 2 inches in outside diameter, for use in 12-liter distillations, to a small size that is 30 millimeters in outside diameter. The column is used as part of an apparatus that is employed extensively for determining the boiling-point ranges of the chemicals listed in the catalog, *Eastman Organic Chemicals*.